Testing Room-Temperature Ionic Liquid Solutions for Depot Repair of Aluminum Coatings

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Prescribed by ANSI Std Z39-18

Outline

A. Background of need
B. Incumbent coating process
C. Ionic liquids technology
D. Ionic liquids for aluminum deposition
E. Coating acceptance criteria
F. Technical challenges and process development
G. Summary

Background

An aluminum electrodeposit on a high-strength steel coupon. The deposit was produced using an ionic liquid electrolyte containing a dissolved aluminum salt.

- Aluminum (Al)
  a) Suitable replacement for cadmium
  b) Has a standard electrode potential of -- 1.676 volts versus the normal hydrogen electrode
  c) Requires specialized processing -- impossible to obtain the electrodeposition of aluminum from an aqueous solution (water hydrolyzes)

Drivers

- Need to repair Al coatings
  a) Pure (> 99%) Al coating electrodeposit
  b) Steel part surfaces
  c) Coating is not all within the line of sight
- Two major requirements:
  a) The repair process must comply with a facility's environment, safety and occupational health (ESOH) requirements
  b) The coating must conform with MIL-DTL-83488, "Detail Specification Coating, Aluminum, High Purity"

Incumbent Aluminum Coating

- Original equipment manufacturers (OEMs) use incumbent Al coating on the part
  - Serves as a cadmium coating replacement
  - Al coating itself is considered to be safe
- Incumbent Al coating technology poses processing issues for a repair facility’s operation
  - Plating bath and its fumes ignite spontaneously in air
  - Stringent controls are required to eliminate moisture contact and mitigate the fire hazard in the facility
  - Currently only plated at coating vendor’s facilities
  - Weeks of delay in plating due to outsourcing

Ionic Liquid: Definition

An "ionic liquid" (IL) is a salt in the liquid state

- Discussion will be limited to a "room-temperature IL" (RTIL), which has a melting point that is less than 100 C
- For example, "BMIM-PF_6" is an RTIL; table salt is not

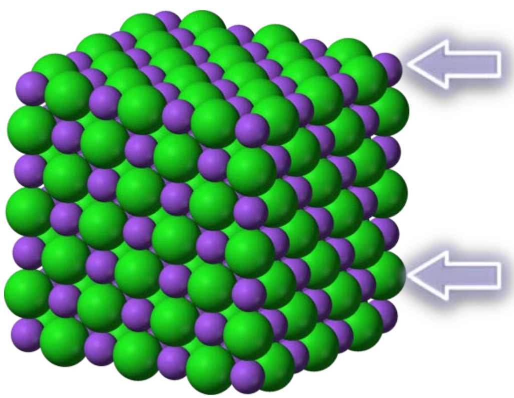
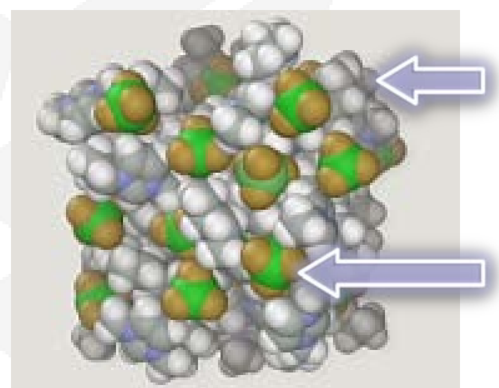


Table Salt (NaCl) Crystal
Melting Point = 801 C

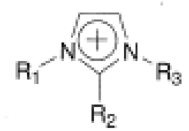
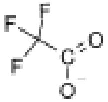
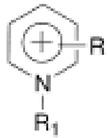
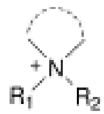
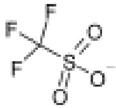
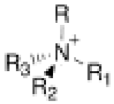
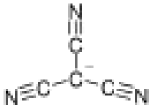
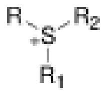
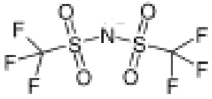


Ionic Liquid (BMIM-PF_6)
Melting Point = 11 C

RTIL Features

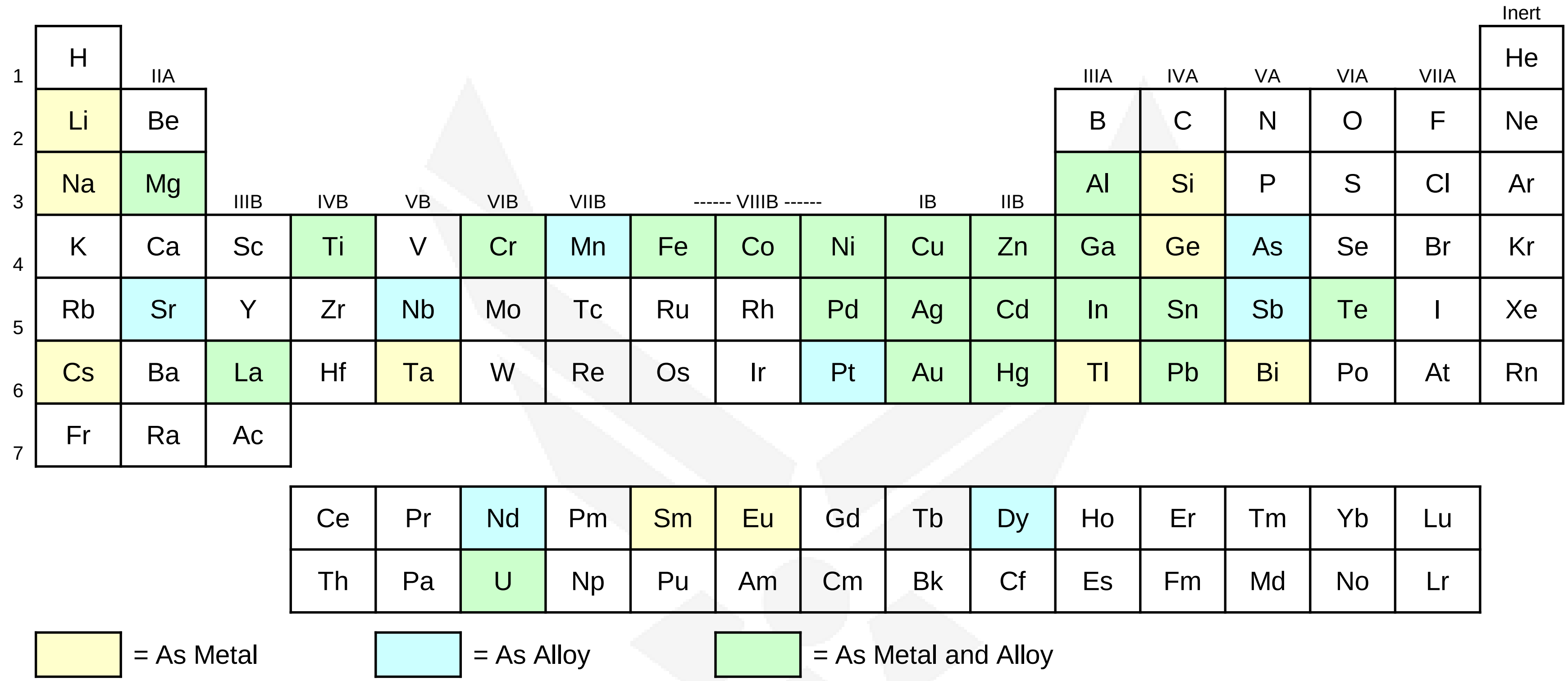
- High solvency (i.e., electrolyte for metal salt)
- Negligible vapor pressure (no VOC issues)
- Non-flammable
- Remain liquid within a wide temperature range
- Other properties may be tailored by the anion/cation selection
    - Physicochemical properties
    - Electrochemical properties

Example RTIL Anions/Cations

Cations		Anions	
Alkylated imidazolium		Trifluoroacetate	
		Bromide	(Br$^-$)
		Chloride	(Cl$^-$)
Alkylpyridinium		Hexafluorophosphate	
Dialkylpyrrolidinium / Dialkylpiperidinium		Tri-fluoromethane sulfonate	
Tetraalkylammonium		Tricyanomethide	
Tetraalkylphosphonium		Tetrafluoroborate	
Trialkylsulfonium		Bis(trifluoromethyl sulfonyl)imide	

- Listing is not comprehensive, particularly for anions
- Dissolving additives into the RTIL adjusts electrolyte properties further

Claimed Plating Opportunities



Reference: Endres, F., A.P. Abbott, and D.R, MacFarlane, Ed., “Electrodeposition from Ionic Liquids,” Wiley-VCH, Weinheim, Germany, 2008.

- **Opportunity of new plating alloys (e.g., Nb)**
- **Plating of active elements (e.g., Mg, Mo, Ta, Ti)**
- **Quality of plating is not quantitatively reported**

Select Al Electroplating in RTIL

- Based options on the research literature
  - Cation
    - Dialkyimidazolium
    - Tetraalkylammonium
    - Tetraalkylphosphonium
    - Dialkylpyrrolidinium
  - Anion
    - Chloride
    - Bis(trifluoromethylsulfonyl)imide (“TFSI”)
- Based selection on commercial availability
  - 1-ethyl,3-methylimidazolium chloride ([EMIM]Cl)

Electroplating Al in [EMIM]

- Aluminum chloride ($AlCl_3$) dissolves in [EMIM]Cl, forming [EMIM] chloroaluminates:

  $$[EMIM]Cl + AlCl_3 \rightarrow [EMIM]AlCl_4,$$
  $$[EMIM]AlCl_4 + AlCl_3 \rightarrow [EMIM]Al_2Cl_7$$

  - Electrolyte is supplied pre-mixed

- Al is plated (Al↓) when there are more dissolved Al atoms than EMIM molecules:

  $$4[EMIM]Al_2Cl_7 + 3e^- \rightarrow Al\downarrow + 4[EMIM]AlCl_4 + 3AlCl_4^-$$

  - 100% plating efficiency at 4 amperes/decimeter^2 (A/dm^2) has been claimed

Al Plating from RTIL Electrolyte

Overview:

1. Remove soils/corrosion products/plating from surfaces
2. Activate the substrate (standard method); dry
3. Electroplate Al onto the activated areas:
   - Pure Al anodes
   - Elevating electrolyte temperature above room temperature (~90°C) improves activity
   - Mechanical agitation
   - Current density of 4 A/dm^2 (example)
4. Rinse and dry plating; Inspect the plating quality

Plating Candidates

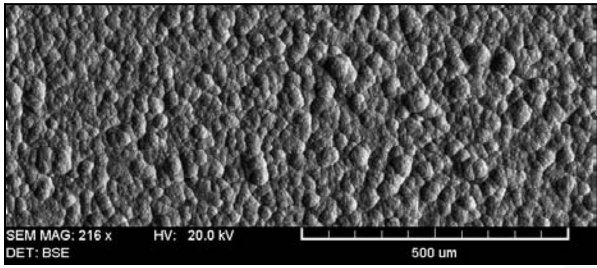
1. Ionic liquid #1, to be used at *CTC* in evaluating processing scale-up at a depot and also submitted for plating tests
2. Ionic liquid #2, plated by a vendor
3. Ionic liquid #3, plated by a vendor; aluminum-zirconium (Al-Zr) alloy
4. Incumbent Al coating, as a baseline
5. Ion Vapor Deposition (IVD) Al, another baseline

Coating Screening Acceptance Criteria

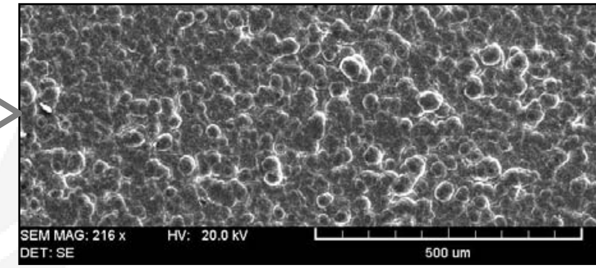
Quality (MIL-DTL-83488)	Coating must be smooth, fine grained, adherent, uniform in appearance, free from staining, pitting, and other defects; coating must show no excessively powdery or darkened areas
Corrosion (ASTM B117)	Specimens shall show no evidence of corrosion of the base metal for a minimum of 504 hours, as specified in Table 1 of MIL-DTL-83488 for Class 1, Type I coatings. Additionally, the appearance of white corrosion products on the Al coating during the test period shall not be cause for rejection.
Thickness (ASTM B499 & ASTM B487)	Al coatings shall be applied to a minimum thickness of 0.0010 in (1 mil), but no greater than 0.0015 in (1.5 mil)
Adhesion (Bend) (ASTM B571)	No separation of the coating from basis metal at interface shall be evident when examined at a minimum of 4X magnification (as per Section 4.4.2.2 of MIL-DTL-83488)
Porosity	Fewer identified pores on average than the average number of pores in baseline panels

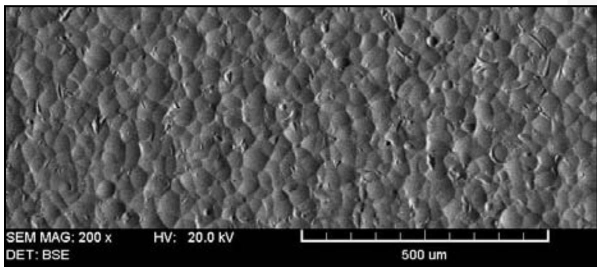
Coating Morphology (ASTM B-487)

Back-Scattered Electron | **Secondary Emission**

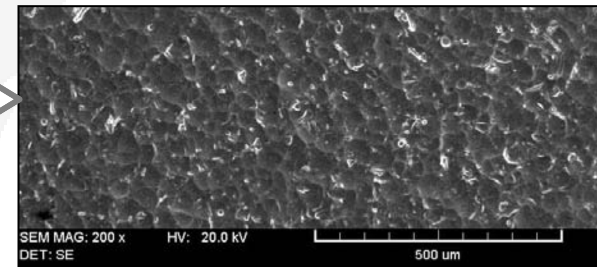


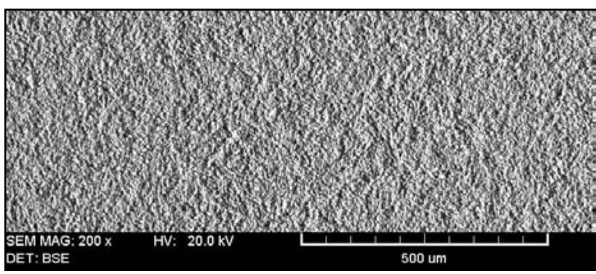
Incumbent at 200X
(as-plated)
>99% Al





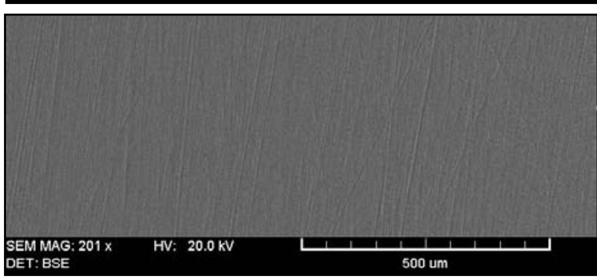
IVD Al at 200X
(glass shot peened)
>99% Al



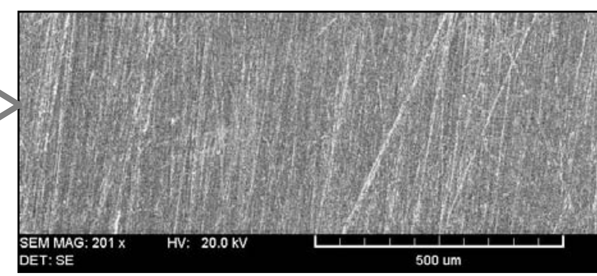


Alternative IL#1 at 200X
(as-plated, preliminary)
>99% Al

(not tested)

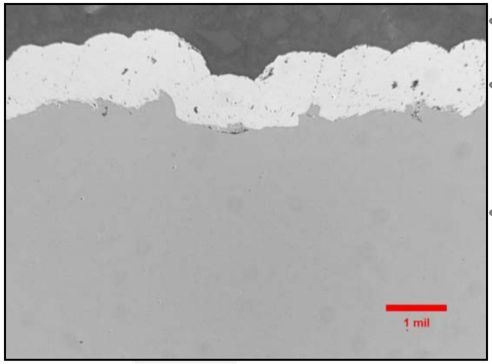


Alternative IL#2 at 200X
(scuffed, preliminary)
>99% Al



Cross-Sectional Analysis (ASTM B-487)

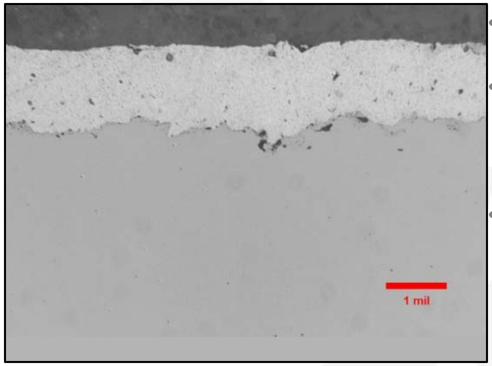
Incumbent Coated Panel at 500X



Mount
Coating
Substrate

Statistics	(Mil)
Minimum:	0.940
Maximum:	1.270
Mean:	1.110
Std Dev.:	0.133

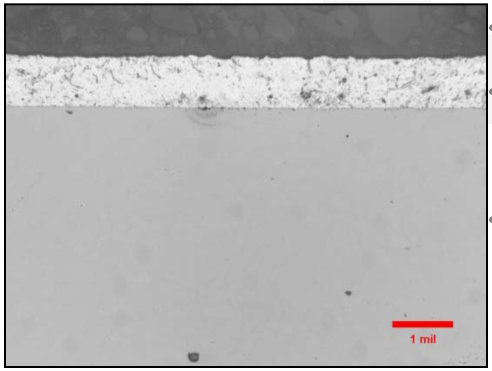
IVD Al Coated Panel at 500X



Mount
Coating
Substrate

Statistics	(Mil)
Minimum:	1.110
Maximum:	1.630
Mean:	1.440
Std Dev.:	0.245

Alternative IL #2 Coated Panel at 500X



Mount
Coating
Substrate

Statistics	(Mil)
Minimum:	0.570
Maximum:	1.070
Mean:	0.802
Std Dev.:	0.217

Al Plating from RTIL Electrolyte Status

- *CTC* is resolving issues with coating thickness and adhesion via in-house IL #1 plating
  - Adjusting agitation to improve coating thickness uniformity
  - Adjusting pretreatment if necessary to improve adhesion consistency
  - Adding filtration to control debris in the bath
- Identifying electroplating equipment required to plate aluminum from RTIL
  - Investigating use of tank liners vs. Teflon® tanks
  - Evaluating inert gas blankets and liquid seals for environmental isolation
  - Examining importance of timing between processing steps

Adhesion (ASTM B-571 Modified)

Panel S-9

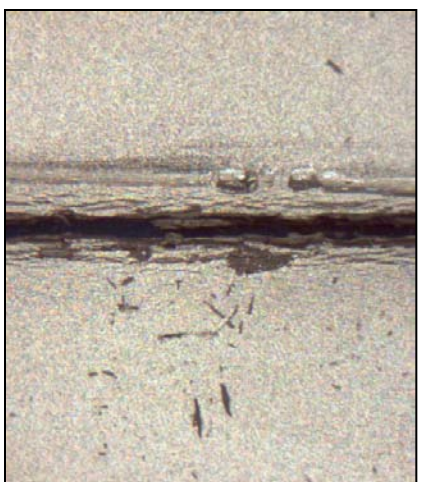
Panel S-10

Panel S-11

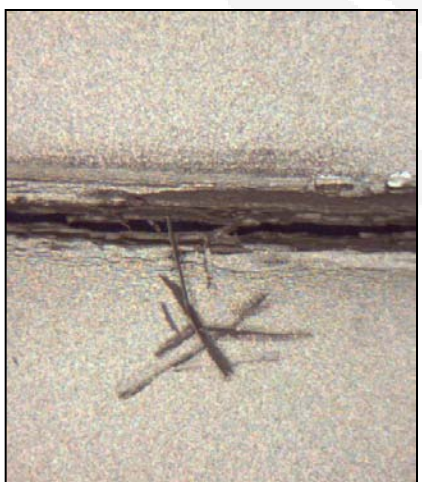
IVD Al Coating

3-Point Bend

(PASS)



Panel S-9



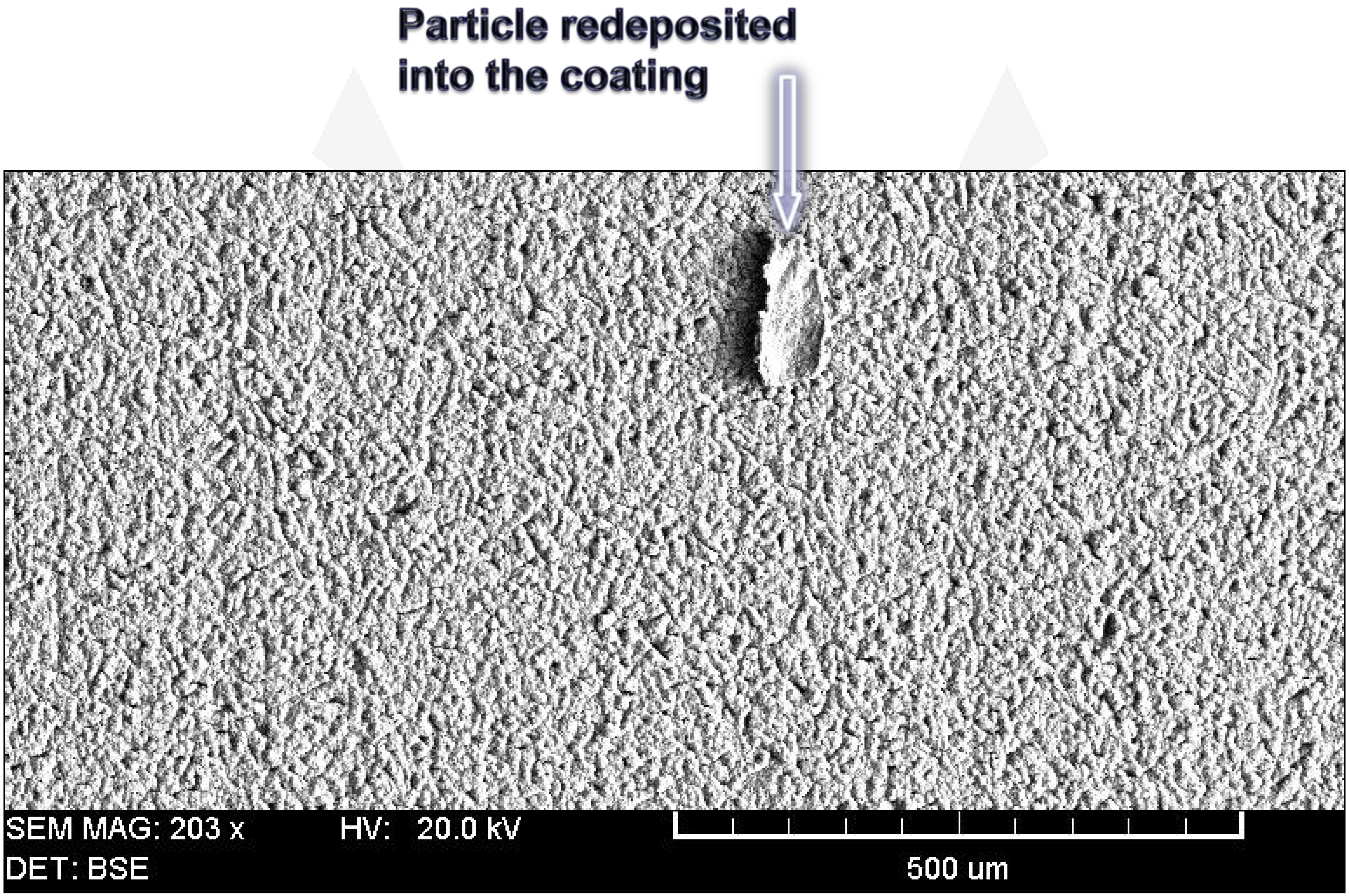
Panel S-10

Panel S-11

Bend-to-Break

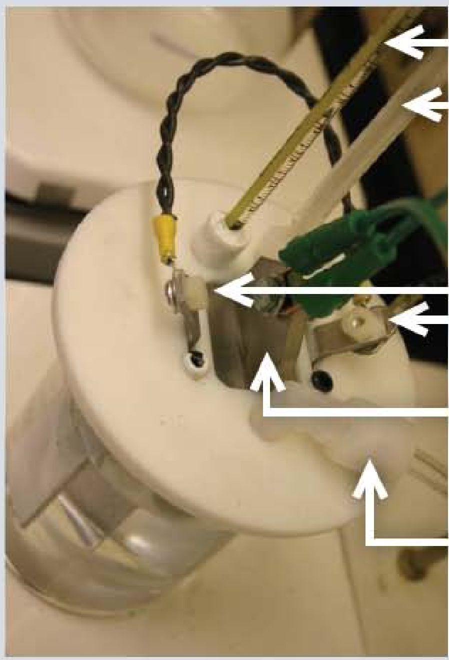
(FAIL)

The Need for Particle Filtration



Details of 1-Liter Test Cell Arrangement

Electroplating Bath Lid Arrangement



Thermometer

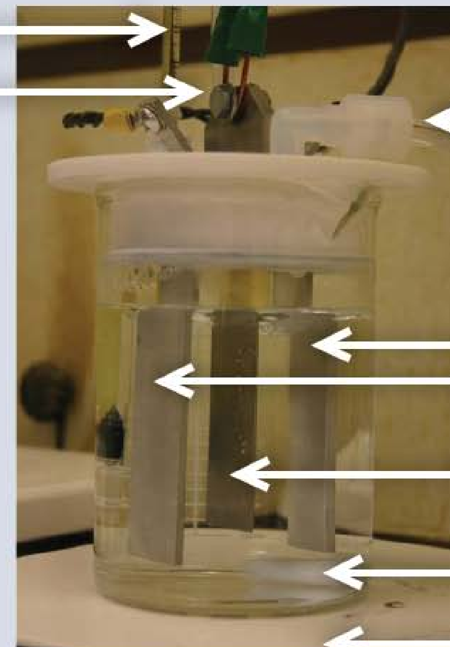
Purge gas vent

Anode lead

Cathode lead (Extractable from the lid)

Purge feed gas

Electroplating Ionic Liquid Bath Set-up



Thermometer

Purge gas vent

Purge gas feed

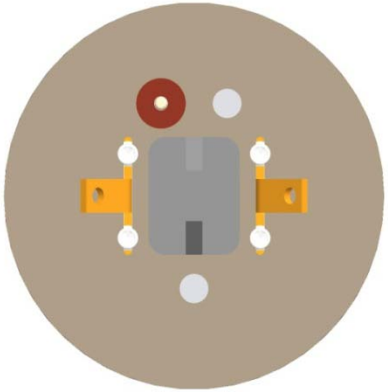
Anode (pure Al)

Cathode (steel)

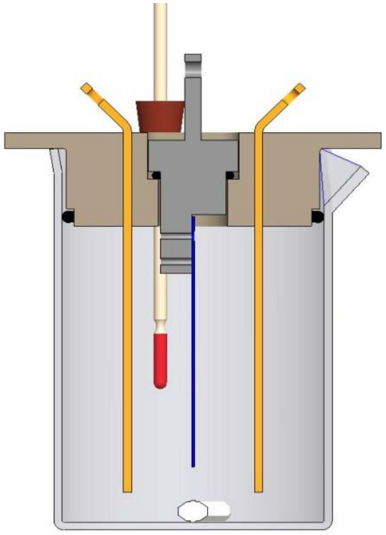
Mixing stir

Hot plate

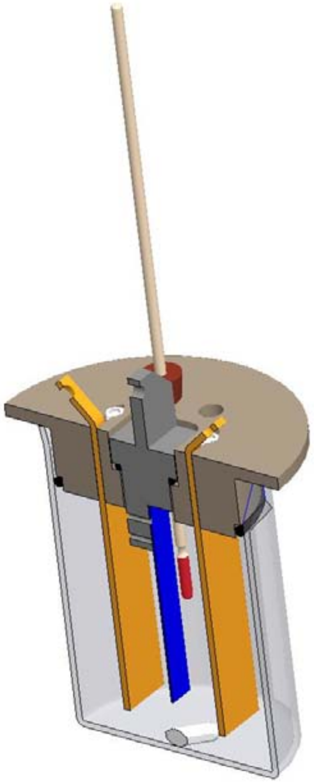
Tooling Views of Lid for 1-Liter Test Cell



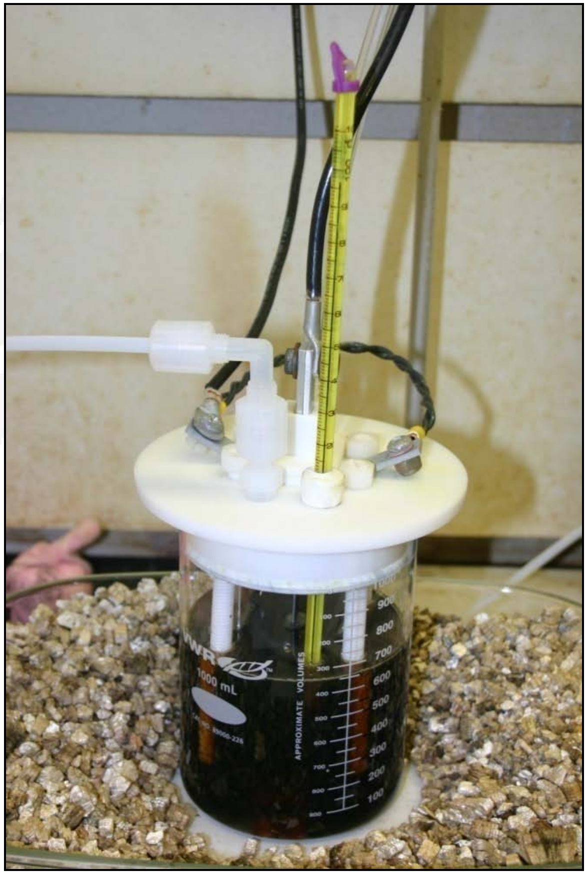
Top View



Side View



Rotated View

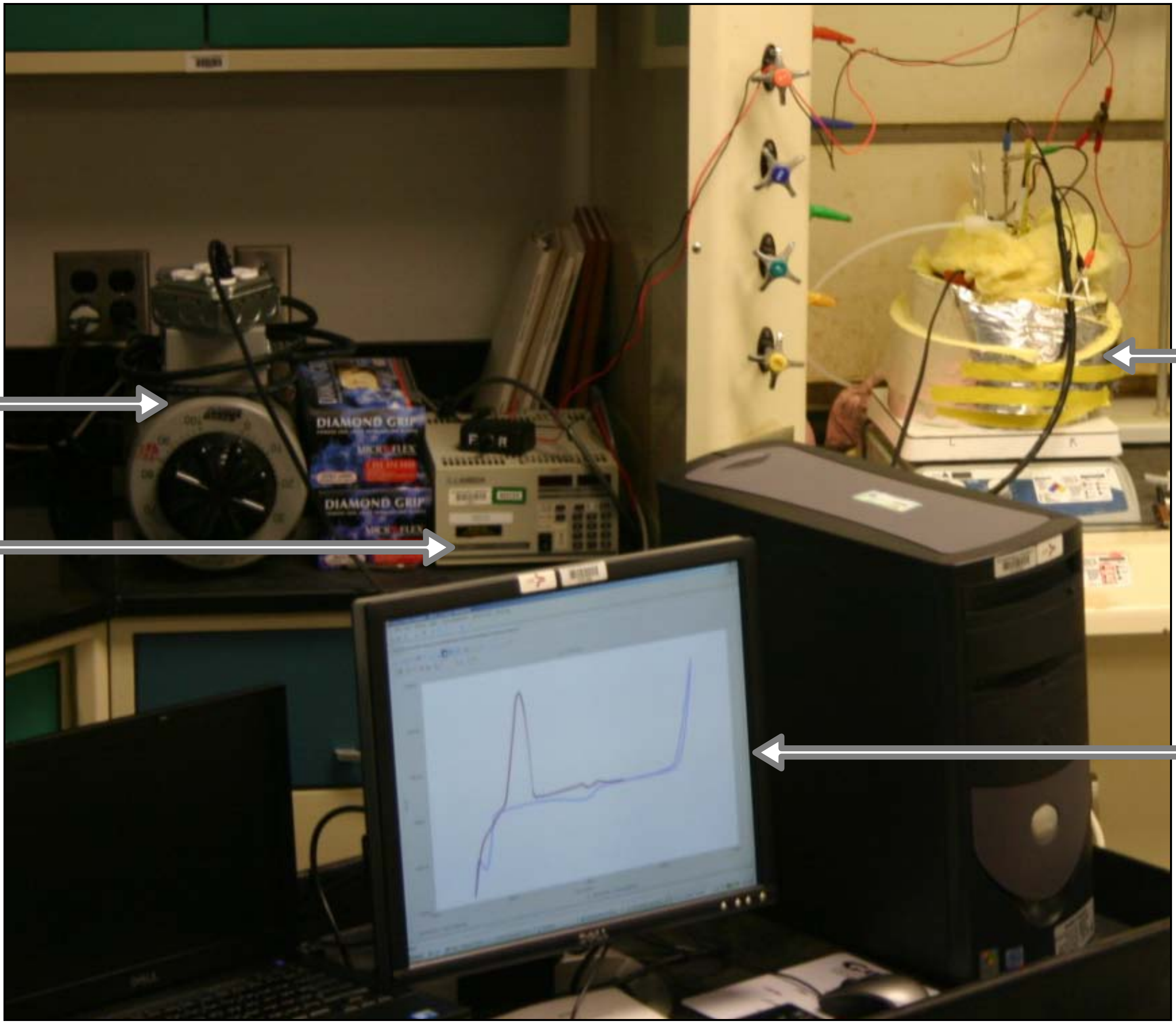


Ionic liquid containing a dissolved aluminum salt

Electroplate Arrangement for 1-Liter Test Cell

Resistance heat variable transformer

Power supply

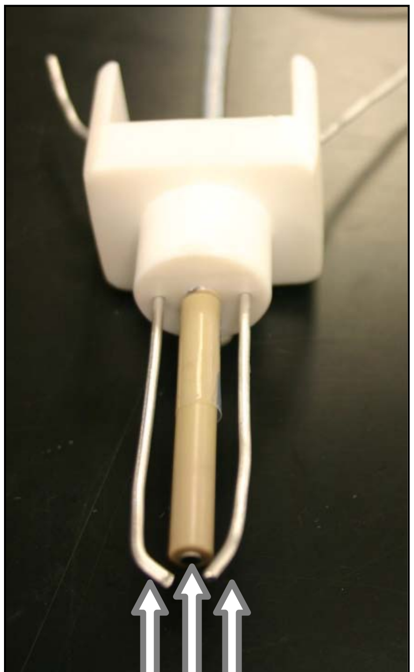


1-liter test cell (insulated)

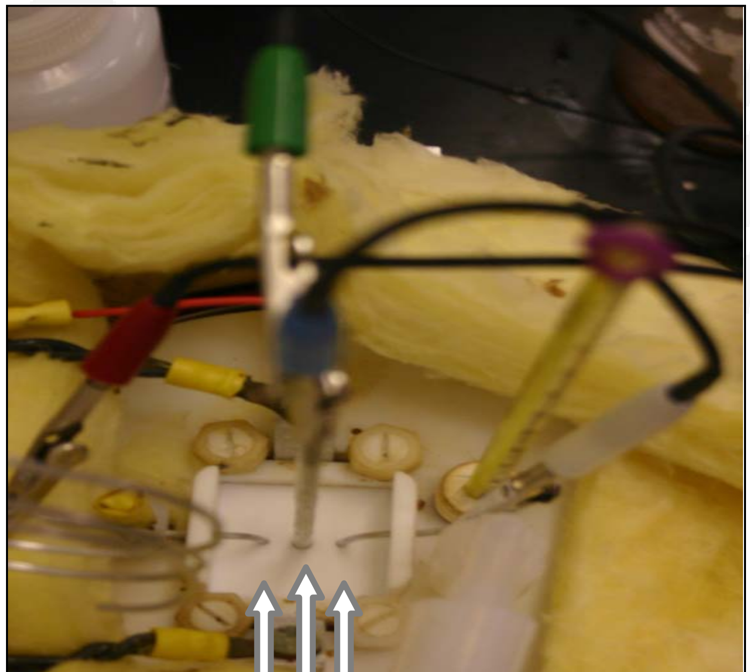
In-situ cyclic voltammetry

Cyclic Voltammetry for RTIL Contamination

Electrodes (3) Arranged in Lid Insert



Electrodes (3) Arranged in Lid Insert in Plating Solution, Connected to Potentiostat Leads

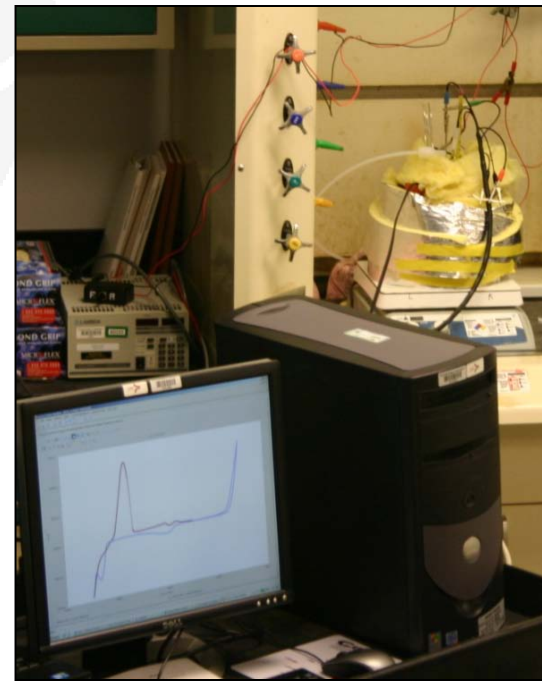


Counter electrode (Al)

Working electrode (Pt)

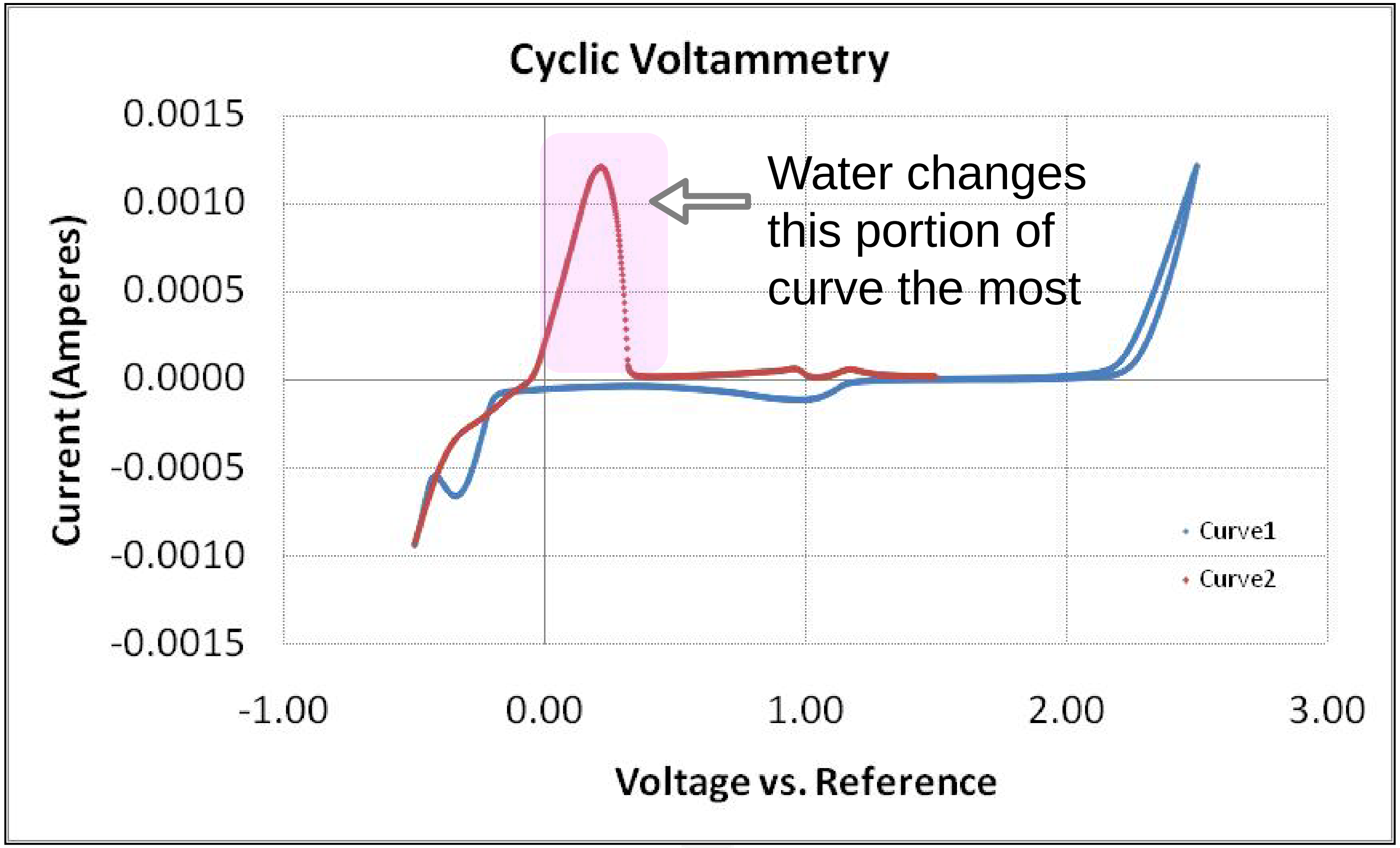
Reference electrode (Al)

Cyclic Voltammetry Measurement In-Situ for Al Plating Solution



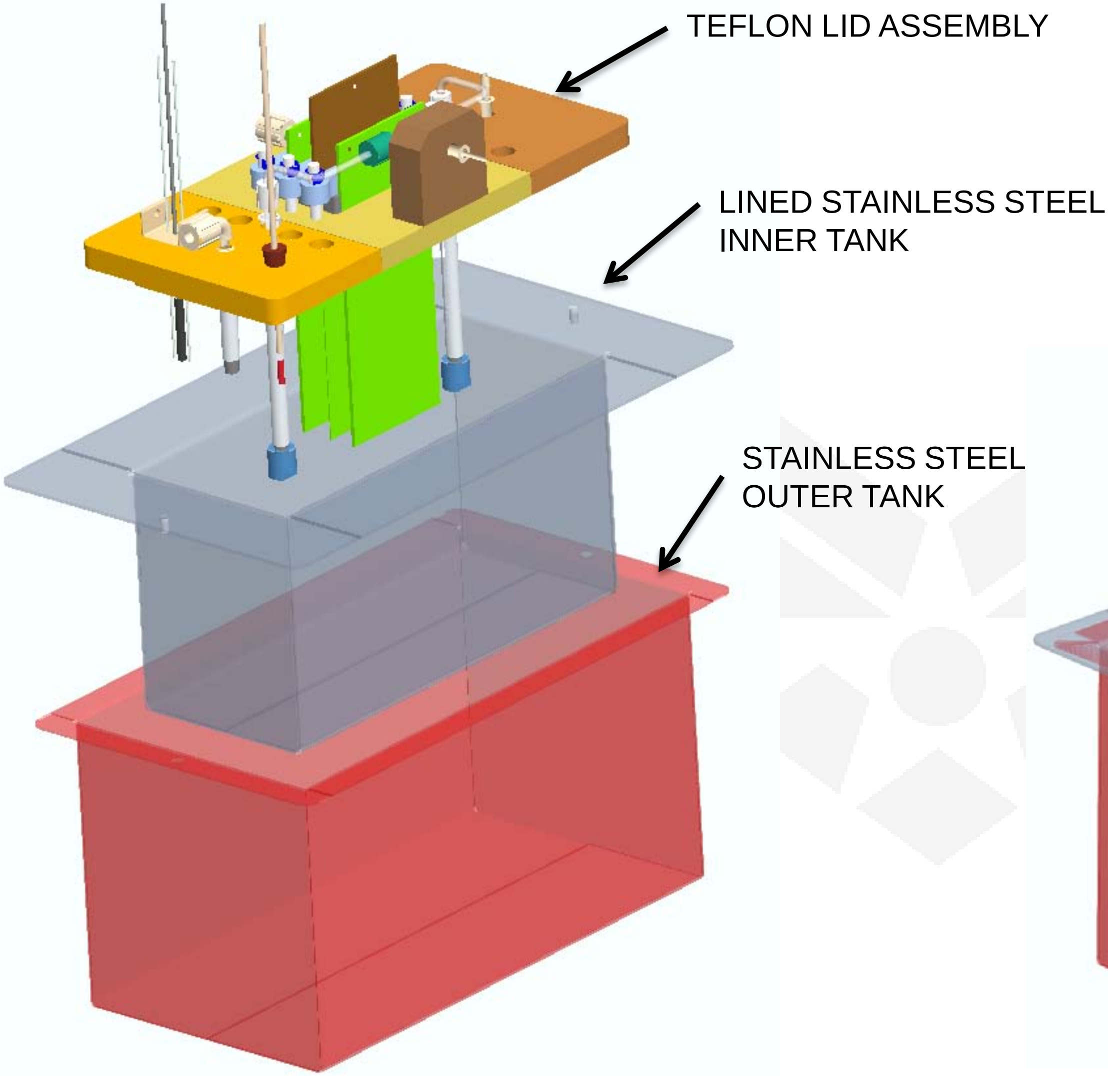
- Room temperature
- No agitation
- 0.07 cm^2 Pt disk area
- 100 mV/s scan rate

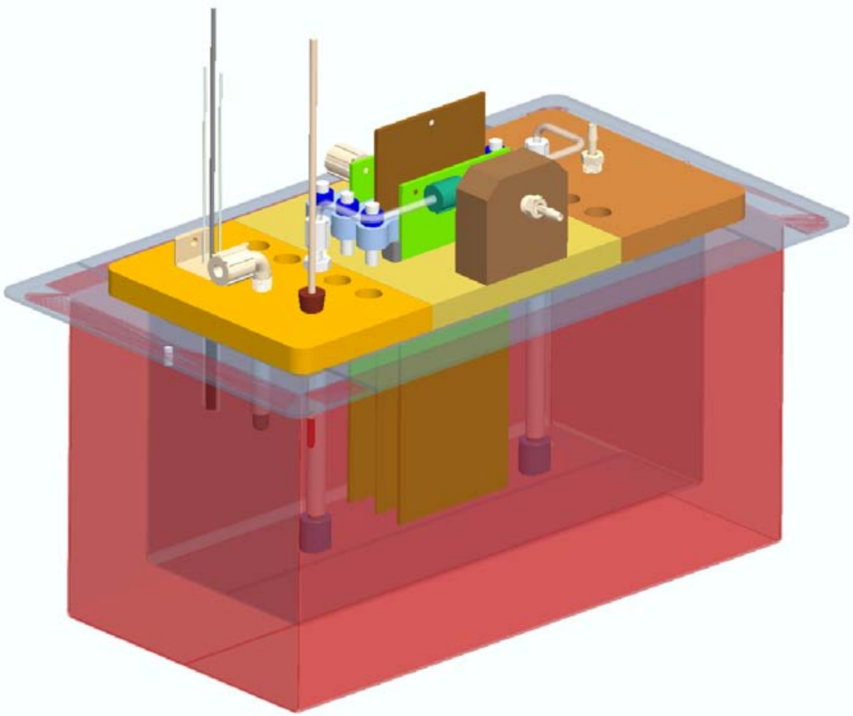
Cyclic Voltammetry for RTIL Contamination



- indication of water contamination is observed via shape changes to the voltammogram, particularly that of the shaded section versus the voltammogram of the fresh electrolyte

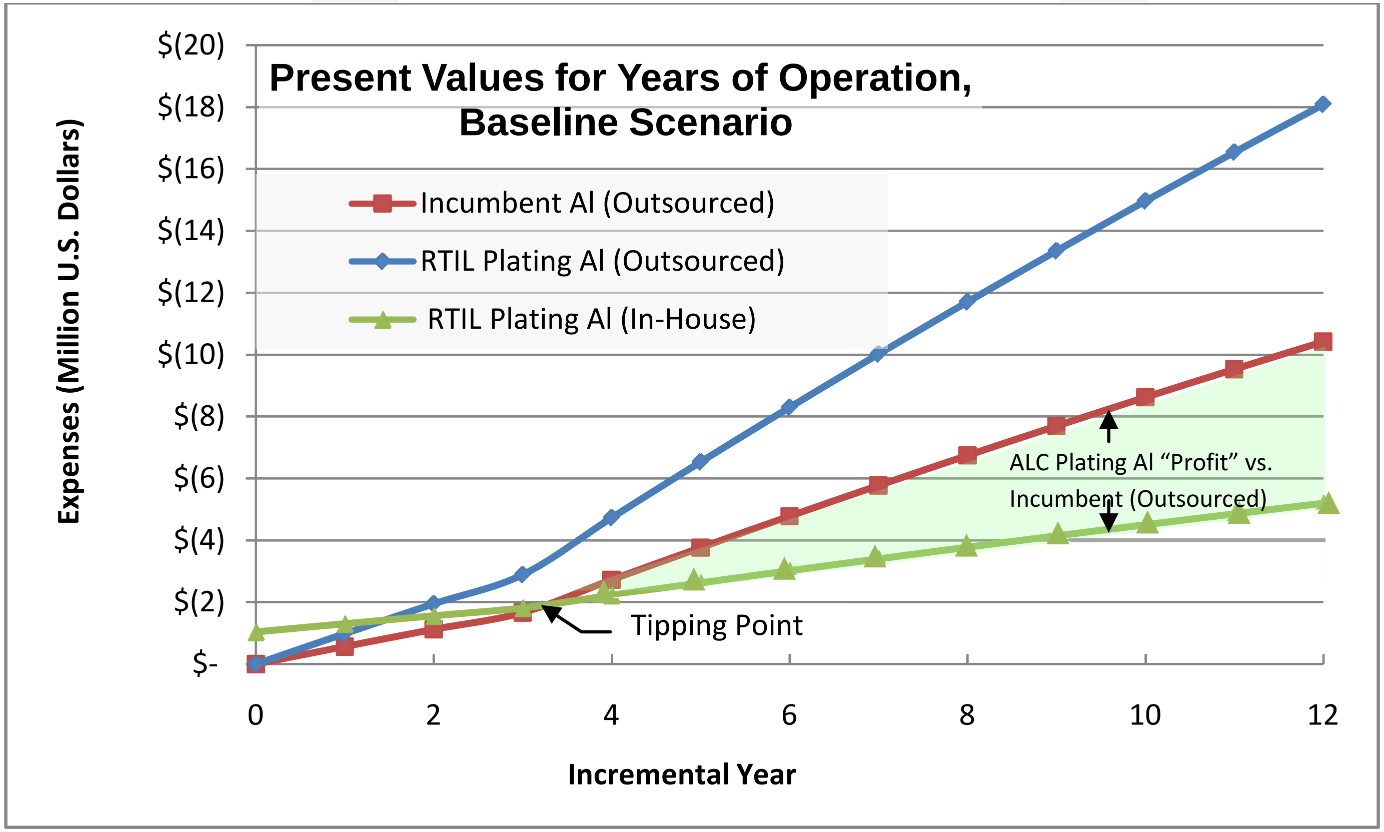
Scale-up to Rectangular Tank





Initial Cost-Benefit Analysis

- ALC plating Al remains financially favored after the 4th year, even with modified or new plating system installation ($1 million capital cost estimated)
- Cumulative present value savings = $5 million during 12 years operation



Note: Continuing search for "more defendable" cost data, which can be rapidly plugged into spreadsheet for updated CBA

Safety Considerations: Primarily Water

1. Water (H_2O) contamination
   - Reacts with chloroaluminate ($AlCl_4^-$) anions:

     $$AlCl_4^- + H_2O \rightarrow AlOCl_2^- + 2HCl\uparrow$$

   - Liberates hydrogen chloride (HCl) gas
   - Forms oxychloroaluminate ($AlOCl_2^-$))
     - Slows plating rate; requires $AlCl_3$ additions
     - Build-up of $AlOCl_2^-$ requires recycling
   - Design limits H_2O contamination
     - Process allows for < 0.1 % H_2O by weight

Safety Considerations (continued)

2. Voltage excursion above ~2.7 volts
   - Chloride anion oxidizes to chlorine at anode: $4AlCl_4^- \rightarrow 2Al_2Cl_7^- + Cl_2\uparrow + 2e^-$.
3. Candidate RTIL electrolyte handling
   - Electrolyte is a superacid
   - Plating bath operates at ~90 C
   - Personal protective equipment is required
     - Face shield, goggles
     - Nitrile gloves with elbow extension

- Hands-on experience indicates hazards are manageable

Summary

1. AFRL/RXSCP and *CTC* are investigating a method for a depot to repair electroplated aluminum, using a near-commercial RTIL electrolyte, [EMIM]Cl-$AlCl_3$.
2. Al coatings are suitable cadmium replacements and lack watch-list chemicals like nickel.
3. RTILs offer the potential of a non-line-of-sight operation that is superior to spray coatings such as IVD Al plating.
4. The current test criteria for coatings produced from RTIL electrolyte are in conformance with the specification for pure aluminum deposits, MIL-DTL-83488.

Summary (continued)

5. Competitive plating rates have been achieved.
6. Adoption of this RTIL process at an ALC avoids outsourcing delays.
7. Preliminary CBA shows cost savings over alternatives.
8. As part of the processing activity, compliance with ESOH requirements are under preliminary review, including designs for container covers.
9. Process development is an ongoing effort; this is not currently an off-the-shelf technology for depot repair.
10. Testing of other ionic liquid technologies is pending.

Future Work

- Completing coating tests to confirm viability
- Examining more complicated geometries that are representative of aircraft
  - Hollow tubes with blind ends
  - Pins for hydrogen embrittlement testing
- Examining alloys based on aircraft applications
  - Fe-Co-Ni alloy, UNS K92580
  - Aluminum-bronze alloy, UNS C63000
  - Alloy Steel, UNS G41400
- Focusing tests on field-oriented needs, for example, strip-and-repair for a depot

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